5. PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL

5.1 PRODUCTION

Polybrominated Biphenyls. The commercial production of PBBs generally involves bromination of biphenyl, a process that involves a much more specific reaction and produces a smaller number of product mixtures than chlorination (Sundstrom et al. 1976a). In one process, biphenyl is brominated with 0–20% stoichiometric excess of bromine chloride (e.g., slightly more than 10 mol of bromine chloride may be reacted with 1 mol of biphenyl to obtain decabromobiphenyl) in the presence of iron or a Friedel-Crafts catalyst (e.g., aluminum chloride). In another process, biphenyl is dissolved in ethylene bromide solvent and reacted with bromine in the presence of a catalyst (either aluminum chloride or bromide) (Neufeld et al. 1977). Research quantities of PBBs can be synthesized by the diazo coupling of brominated aniline with an excess of the corresponding bromobenzene. For example, 2,3,3',4,4',5'-hexabromobiphenyl can be synthesized by the diazo coupling of 3,4,5-tribromoaniline with 1,2,3-tribromobenzene (Kubiczak et al. 1989; Robertson et al. 1983b). Methods for laboratory scale synthesis of 42 congeners of brominated biphenyls are also available (Sundstrom et al. 1976b).

The commercial production of PBBs began in 1970. Approximately 13.3 million pounds of PBBs were produced in the United States from 1970 to 1976. Only three commercial PBB products were manufactured (i.e., hexabromobiphenyl, octabromobiphenyl, and decabromobiphenyl) and these three products were based on a limited number of congeners (Hardy 2002). Hexabromobiphenyl constituted about 11.8 million pounds (ca 88%) and octa- and decabromobiphenyl constituted . 1.5 million pounds together of this total (Neufeld et al. 1977). Over 98% of the hexabromobiphenyl was produced as FireMaster BP-6 and the residual as FireMaster FF-1 (Hesse and Powers 1978). Michigan Chemical Corporation, St. Louis, Michigan, the sole producer of hexabromobiphenyl in the United States, stopped producing this PBB in 1975. White Chemical Co., Bayonne, New Jersey, and Hexcel Corporation, Sayreville, New Jersey, manufactured octa- and decabromobiphenyl in the United States until 1979 (IARC 1986; Neufeld et al. 1977). Shortly after the 1973–1974 agriculture contamination episode in Michigan (see Section 3.2), PBB production in the United States was voluntarily discontinued (Hardy 2000); PBBs are no longer produced in the United States (SRI 2001). Re-initiation of manufacture requires approval from the EPA. Production of decaPBB in Great Britain was discontinued in 1977 and highly brominated PBBs were produced in Germany until mid-1985. Until the year 2000, the only PBB in commercial production was decabromobiphenyl, which was manufactured by one company (Atochem) in France (Hardy 2000).

Polybrominated Diphenyl Ethers. The commercial production of PBDEs generally involves bromination of diphenyl oxide to varying degrees. The degree of bromination is controlled either through stiochiometry or through control of reaction kinetics (Pettigrew 1993). Technical decabromodiphenyl ether is manufactured by bromination of diphenyl oxide in the presence of a Friedel-Crafts catalyst (e.g., aluminum bromide) and excess bromine. Technical decabromodiphenyl ether may also be produced at atmopsheric pressure by dissolving diphenyl oxide and bromine in ethylene dibromide in the presence of a Friedel-Crafts catalyst (e.g., aluminum bromide). The use of bromine in an organic solvent requires long reaction times, results in low productivity per volume, and necessitates recycling of the solvent. These limitations have led to the use of bromine as both the reactant and the solvent for this process (Dagani and Sanders 1985).

The commercial production of PBDEs began in late 1970s (WHO 1994a). In the United States, penta-, octa-, and decabromodiphenyl ethers are produced at Albemarle Corporation, Magnolia, Arkansas, and Great Lakes Chemical Corporation, El Dorado, Arkansas (SRI 2001). Technical OBDE is produced commercially in the United States as DE-79, FR-1208, and Saytex 111. Technical PeBDE is produced commercially in the United States as Bromkal 70-5DE, DE-71, Tardex 50, Tardex 50 L, and Saytex 115. Technical DeBDE (BDE-209) is produced commercially in the United States as DE-83, FR-300 BA, Saytex 102 (see Section 4.1). Six manufacturers are currently producing polybrominated diphenyl ethers in other countries: Dead Sea Bromines/Eurobrome (The Netherlands); Atofina (France); Tosoh (Japan); Matsinaga (Japan); Nippo (Japan); and Great Lakes Chemical Ltd (United Kingdom) (WHO 1994a). No current estimates of PBDE production are available (SRI 2001). In 1999, the total market demand for PBDEs in the United States was 74.9 million pounds. Technical decabromodiphenyl ether constituted about 53.6 million pounds (72%), while technical mixtures of octa- and pentabromodiphenyl ethers were 3.0 and 18.3 million pounds (4 and 24%) of this total, respectively (BSEF 2002).

Table 5-1 lists the facilities in each state that manufacture or process technical decabromodiphenyl ether (DeBDE), the intended use, and the range of maximum amounts of technical DeBDE that are stored on-site. There are 144 facilities that produce or process technical DeBDE in the United States (TRI99 2001). The data from the Toxics Release Inventory (TRI) listed in Table 5-1 should be used with caution, however, since only certain types of facilities were required to report. The TRI is not an exhaustive list.

Table 5-1. Facilities that Produce, Process, or Use Decabromodiphenyl Ether

State[a]	Number of facilities	Minimum amount on site in pounds[b]	Maximum amount on site in pounds[b]	Activities and uses[c]
AL	1	10,000	99,999	7, 8
AR	4	1,000	9,999,999	1, 4, 7, 8
CA	5	1,000	999,999	7, 8
CT	4	1,000	99,999	7, 8, 9, 14
FL	1	100,000	999,999	7
GA	4	100	99,999	7, 8
IL	2	10,000	99,999	7, 8
IN	5	0	999,999	7, 8
KS	1	100	999	11
KY	2	10,000	999,999	7
LA	1	100,000	999,999	12
MA	12	1,000	99,999	7, 8
MD	1	100,000	999,999	8
MI	6	1,000	9,999,999	1, 3, 7, 8
MN	5	1,000	99,999	6, 7, 8, 9, 12
MO	1	1,000	9,999	7
MS	1	10,000	99,999	7
NC	12	1,000	999,999	7, 8
NE	1	10,000	99,999	8
NH	1	1,000	9,999	7
NJ	3	10,000	999,999	7, 8
NY	3	10,000	99,999	6, 7, 8
OH	9	1,000	999,999	7, 8
OR	1	10,000	99,999	12
PA	8	1,000	9,999,999	7, 8
RI	3	1,000	99,999	7, 8, 10
SC	9	1,000	999,999	7, 8
TN	6	1,000	99,999	7
TX	8	100	99,999	1, 3, 7, 8, 12
VA	5	10,000	999,999	7, 8
WA	1	10,000	99,999	8
WI	2	1,000	9,999	7, 8

Source: TRI00 2002

[a]Post office state abbreviations used
[b]Amounts on site reported by facilities in each state
[c]Activities/Uses:

1. Produce
2. Imported
3. Used Processed
4. Sale Distribution
5. Byproduct
6. Reactant
7. Formulation Component
8. Article Component
9. Repackaging
10. Chemical Processing Aid
11. Manufacture Aid
12. Ancillary/Other Uses
13. Manufacture Impurity
14. Process Impurity

5.2 IMPORT/EXPORT

Polybrominated Biphenyls. PBBs are no longer being imported or exported except possibly in small quantities for laboratory uses. PBBs have not been imported from other countries into the United States, except in finished products (Neufeld et al. 1977). The two companies that manufactured octa- and decabromobiphenyl in the United States between 1976 (0.805 million pounds) and 1978 exported all of their products to Europe (Neufeld et al. 1977).

Polybrominated Diphenyl Ethers. No U.S. import or export data were located in the literature for PBDEs. In 1999, worldwide demand for technical penta-, octa-, and decabromodiphenyl ethers were 18.7 million, 8.4 million, and 121 million pounds, respectively (BSEF 2002).

5.3 USE

Polybrominated Biphenyls. PBBs are no longer used in the United States. In the past, PBBs were used as additive flame retardants used to suppress or delay combustion. Additive flame retardants are added to the polymer material, but are not chemically incorporated into the polymer matrix. Because PBBs are not chemically bound to the polymer matrix, they may migrate out of the matrix with time (WHO 1994b). PBB applications were almost exclusively limited to a particular thermoplastic (arylonitrile-butadiene-styrene, ABS) used in electronic equipment housings (Hardy 2002). Prior to termination of production, hexabromobiphenyl was used as a fire retardant mainly in thermoplastics for constructing business machine housings and in industrial (e.g., motor housing), and electrical (e.g., radio and TV parts) products. Smaller amounts were used as a fire retardant in coating and lacquers, and in polyurethane foam for auto upholstery (Neufeld et al. 1977). PBDEs and other flame retardants replaced hexabromobiphenyl after its voluntary ban in the late 1970s. Octabromobiphenyl and decabromobiphenyl were never used in the United States, probably because the hexabromobiphenyl was less expensive and equally effective as a fire retardant (Neufeld et al. 1977).

Polybrominated Diphenyl Ethers. PBDEs are used as additive flame retardants in thermoplastics. Additive flame retardants are physically combined with the polymer material being treated rather than chemically combined (as in reactive flame retardants). This means that there is a possibility that the flame retardant may diffuse out of the treated material to some extent.

PBDEs are used in different resins, polymers, and substrates at levels ranging from 5 to 30% by weight (EU 2001). Plastic materials that utilize PBDEs as flame retardants include: ABS; polyacrylonitrile

(PAN); polyamide(PA); polybutylene terephthalate (PBT); polyethylene (PE); cross-linked polyethylene (XPE); polyethylene terephthalate (PET); polypropylene (PP); polystyrene (PS); high-impact polystyrene (HIPS); polyvinyl chloride (PVC); polyurethane (PUR); and unsaturated polyester (UPE). These polymers and examples of their final products are summarized in Table 5-2 (Hardy 2002; WHO 1994a).

Currently, technical DeBDE is the most widely used PBDE flame retardant worldwide followed by technical ODBE. About 95% of technical PeBDE is used in the manufacture of flexible polyurethane (PUR) foam for furniture and upholstery. Flexible polyurethane foam is used in foam-based laminated automotive applications, for domestic furniture, and in foam-based packaging (EU 2001). Technical OBDE is mainly used in the preparation of acrylonitrile-butadiene-styrene terpolymer (ABS), which is used in the manufacture of computer and business equipment housings. Technical OBDE is also used in adhesives and coatings applications (WHO 1994a). About 40% of technical DeBDE is used in combination with antimony trioxide in high impact polystyrene applications, such as television and radio housings. Other significant uses of technical DeBDE are in textile applications, such as polyester fiber additives and coatings for automobile fabric, tarpaulins, and tents (WHO 1994a).

5.4 DISPOSAL

Polybrominated Biphenyls. PBBs are no longer commercially produced in the United States. In the past, an estimated 0.0046 pounds have been lost to sewers for every 1,000,000 pounds of PBBs produced at manufacturing sites (Neufeld et al. 1977). The Michigan Chemical Corporation discharged an estimated 0.25 pounds of PBBs/day to the Pine River as effluent (Di Carlo et al. 1978). The Michigan Chemical Corporation estimated that the solid waste generated during the manufacture of FireMaster BP-6 was . 5% of the FireMaster BP-6 and FireMaster FF-1 produced (Di Carlo et al. 1978). Since Michigan Chemical Corporation produced . 11.8 million pounds of Firemaster BP-6 and Firemaster FF-1 from 1970 to 1974 (Di Carlo et al. 1978), solid wastes containing a total of . 590,000 pounds of PBBs would have been sent to disposal. About one-half of this waste was deposited in the Gratiot County landfill in St. Louis, Michigan (Di Carlo et al. 1978), and the rest was possibly landfilled at other locations. Contaminated animal carcasses, poultry and eggs, animal feed, butter, cheese, and other milk products following the Michigan agriculture contamination episode were disposed of in a sanitary landfill in Cadillac, Michigan (Dunckel 1975).

Table 5-2. Uses of Penta-, Octa-, and Decabromodiphenyl Ethers Commercial Mixtures in Resins, Polymers, and Substrates

Resin/polymer/ substrate	Example of final product	Pentabromo-diphenyl ether	Octabromo-diphenyl ether	Decabromo-diphenyl ether
ABS	Molded parts (e.g., TV sets/business machines. computer housings, household appliances [hairdryer, curler], automotive parts, electronics, telecommunications)		•	
Epoxy-resins	Circuit boards, protective coatings (e.g., computer, ship interiors, electronic parts)			•
Phenolic resins	Printed circuits boards (e.g., paper laminates/glass prepregs for circuit boards)	•		•
PAN	Panels, electrical components (e.g., lighting panels for elevators and rooms, housing of electrical appliances)			•
PA	Electrical connectors, automotive interior parts (e.g., computers, connectors, housing in electricl industry, board, electrical connectors, automotive industry, transportation)		•	•
PBT	Electrical connectors and components (e.g., switches fuse, switch box, computer housing, switchboard electrical connectors, stereos, business machines, military electronics)		•	•
PE/XPE	Cross-linked wire and cable, foam tubing, weather protection, and moisture barriers (e.g., power cable, building conduit, portable apparatus building control, instrument, shipboard, automotive, marine appliances, insulation of heating tubes)			•
PET	Electrical components (e.g., boxes, relays, coils, bobbins)			•

Table 5-2. Uses of Penta-, Octa-, and Decabromodiphenyl Ethers Commercial Mixtures in Resins, Polymers, and Substrates *(continued)*

Resin/polymer/ substrate	Example of final product	Pentabromo-diphenyl ether	Octabromo-diphenyl ether	Decabromo-diphenyl ether
PVC	Cable sheets (e.g., wire and cables, floor mats, industrial sheets)	•		•
PUR	Cushioning materials, packaging, padding (e.g., furniture, sound insulation panels, wood imitations, transportation)	•		
UPE	Circuits boards, coatings (e.g., electrical equipment, coatings, military and marine applications, construction panels)	•		•
Rubber	Transportation (e.g., conveyor belts, foamed pipes for insulation)	•		•
Paints/lacquers	Coatings (e.g., marine and industry lacquers for protection of containers)	•		•
Textiles	Coatings (e.g., back coatings, impregnation, carpets, automotive seating, furniture in homes and office buildings, aircraft, subways, tents, trains, and military safety clothing)	•		•

Source: WHO (1994a)

ABS = Acrylonitrile Butadiene Styrene; PA = Polyamide; PAN = Polyacrylonitrile; PBT = Polybbutylene Terephthalate; PE = Polyethylene; PET = Polyethylene Terephthalate; PP = Polypropylene; PUR = Polyurethane; PVC = Polyvinyl chloride; UPE = Unsaturated polyester; XPE = Cross-linked polyethylene;

Approximately 11.8 million pounds of hexabromobiphenyl were used in commercial and consumer products in the United States, most in the production of plastic products with an estimated use life of 5–10 years (Neufeld et al. 1977). Since the cessation of production, all of these products, such as TV cabinet and business machine housings, must have been disposed of by land filling or incineration (Neufeld et al. 1977). The formation of polybrominated dioxins (PBDDs) and polybrominated dibenzofurans (PBDFs) during the incineration of plastics containing PBBs remains a distinct possibility (Luijk and Govers 1992; O'Keefe 1978).

Polybrominated Diphenyl Ethers. PBDEs are used as flame retardants in a wide range of products (see Section 5.3). Waste from these products may be either incinerated as municipal waste, deposited in landfills, discharged to municipal sewage treatment plants, or emitted to the atmosphere. (Darnerud et al. 2001). The disposal of plastic consumables containing PBDEs (e.g., computers) to landfills is likely to increase in the United States due to their limited useful lifespan. No study on leaching of PBDEs from landfills is available. However, PBDE-containing products are widespread and leaching may be an important long-term pathway of contamination. PBDEs are discharged in to the environment through sewage, as indicated by analysis of sewage sludge from various countries. Tetra- and pentaBDE were detected in sewage sludge from publically owned treatment works (POTWs) in the United States (La Guardia et al. 2000). The composition in the biosolids closely resembled the DE-71 commercial formulation.

Although specific data are missing, incineration is thought to be an important route of release of PBDEs into the environment. Formation of PBDFs and/or PBDDs as a result of landfill fires is also a possibility, though no data are available on the scale of this source. The results of pyrolysis experiments showed that PBDEs can form PBDFs and PBDDs (in much smaller quantities) under a wide range of heating conditions. If chlorine is present, mixed halogenated furans/dioxins can be formed (Oberg et al. 1987; Zier et al. 1991). Unless sufficiently high temperatures and long residence times are maintained, PBDFs/PBDDs can be generated during the incineration of products containing PBDEs. When heavy metals are present, the concentration of PBDDs and PBDFs are higher than when no metals are present. However, modern, properly operated municipal waste incineration should not emit significant quantities of PBDFs/PBDDs, regardless of the composition of municipal waste (WHO 1994a).

Solid wastes from the commercial production of technical OBDE, such as filter cakes, are disposed of in hazardous waste landfills (EPA 1994). These wastes may contain toluene from the production process.

No study on leaching of PBDEs from landfills is available, but PBDE-containing products are widespread, and leaching may be an important long-term pathway of contamination. PBDEs are discharged in to the environment through sewage, as indicated by analysis of sewage sludge from various countries. Volatilization of PBDEs into the surrounding air from electrical components and other products during their lifetime can also be significant (Darnerud et al. 2001).

No other information was located on the past or present volumes of PBDEs disposed of by each disposal method.